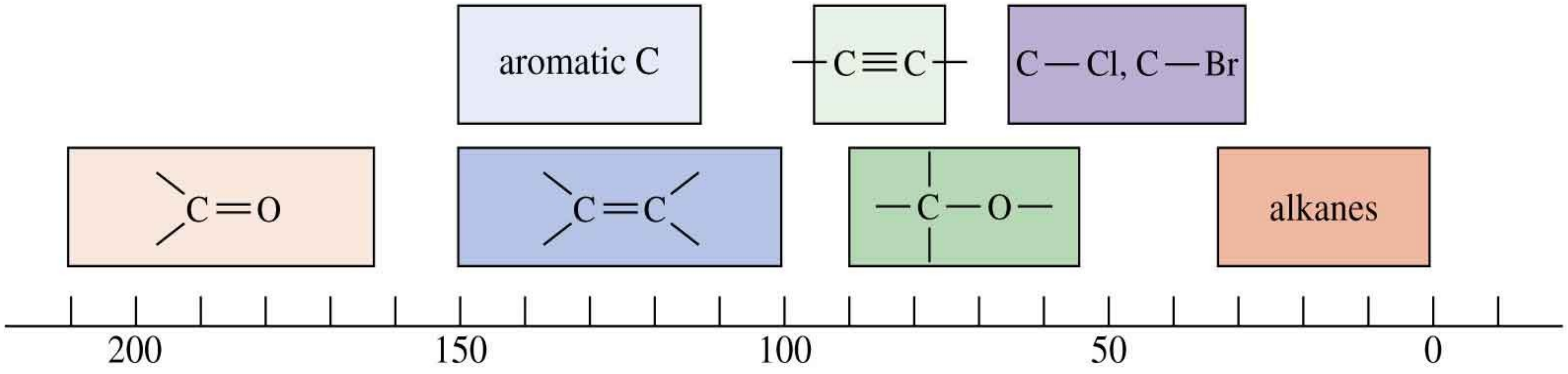
Carbon-13

- ^{12}C has no magnetic spin.
- ^{13}C has a magnetic spin, but is only 1% of the carbon in a sample : 15.1 MHz instead of 60 MHz.
- The gyromagnetic ratio of ^{13}C is one-fourth of that of ^{1}H.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

Hydrogen and Carbon Chemical Shifts



Type of Carbon	Chemical Shift (ppm)	Type of Carbon	Chemical Shift (ppm)
$R-CH_3$	0 – 35	$R_2C=$	80 – 150
R_2CH_2	15 – 55	aromatic C	110 – 170
R_3CH	25 – 55	$RC(=O)OR$	165 – 175
R_4C	30 – 40	$RC(=O)OH$	175 – 185
$-C-X$ (X: Cl, Br or N)	10 – 65	$RC(=O)H$	190 – 200
$-C-O-$	50 – 90	$RC(=O)R$	200 – 220
$R-C\equiv$	70 – 90		

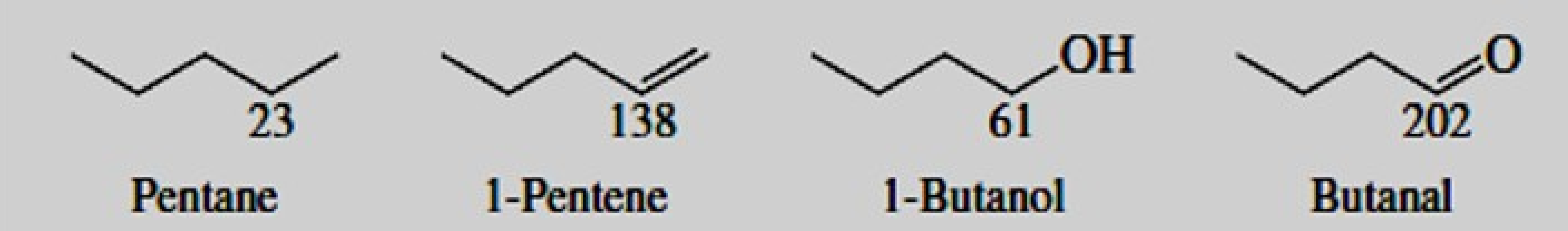
Chemical Shifts

^{13}C signals are spread over a much wider range than ^{1}H signals making it easier to identify and count individual nuclei

^{13}C Chemical shifts are most affected by:

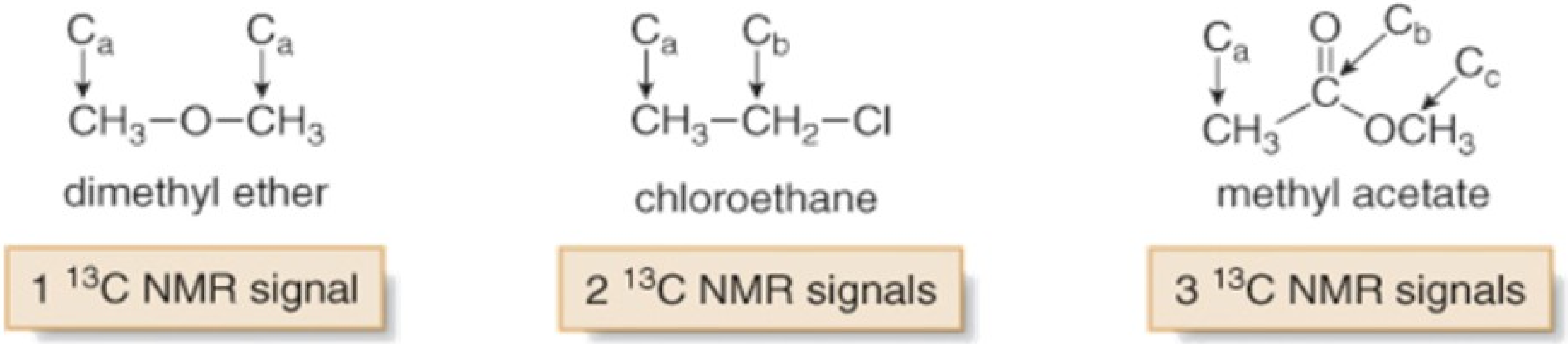
- **hybridization state of carbon.**
- **electronegativity of groups attached to carbon.**

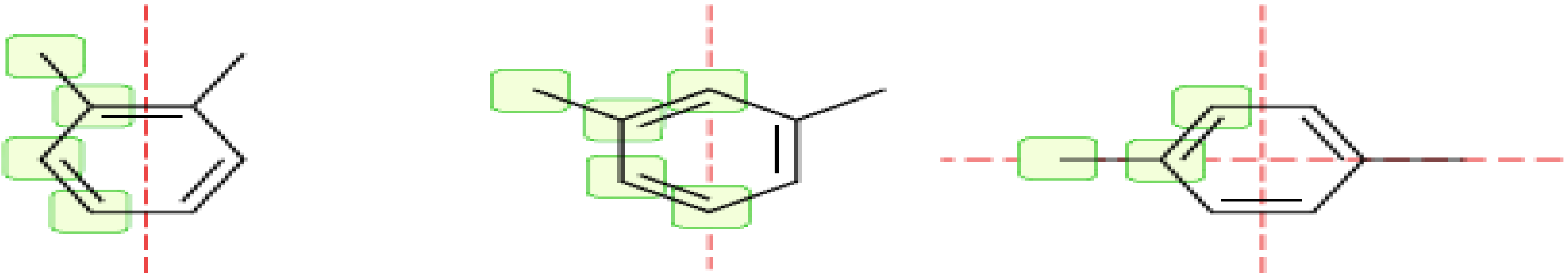
Replacing the methyl group in pentane by the more electronegative oxygen deshields the carbon in 1-butanol. Likewise, replacing C-1 in 1-pentene by oxygen deshields the carbonyl carbon in butanal.



number of signals

The number of signals in a 13C-NMR spectrum represents the number of carbon atoms in different electronic env

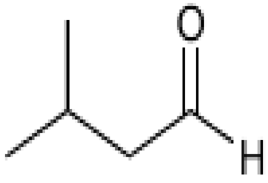


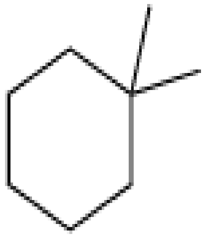


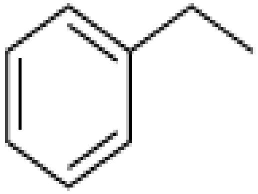
Four signals | Five signals | Three signals

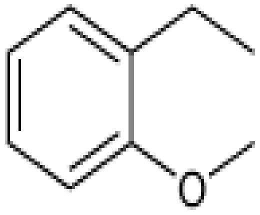
number of signals

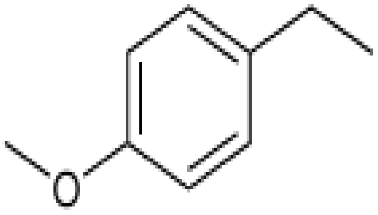
For each of the following compounds, predict the number of signals and the approximate chemical shift of each signal in a 13C NMR spectrum:

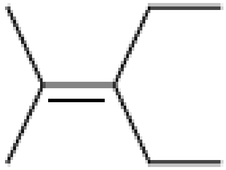
(a) 

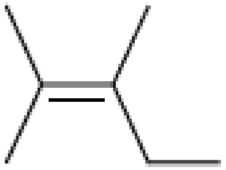
(b) 

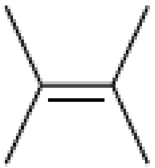
(c) 

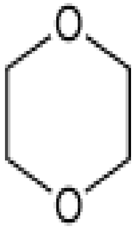
(d) 

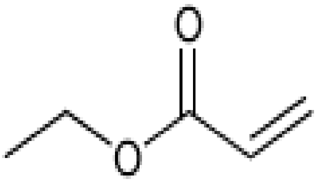
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

Spin-Spin Splitting (proton-coupled)

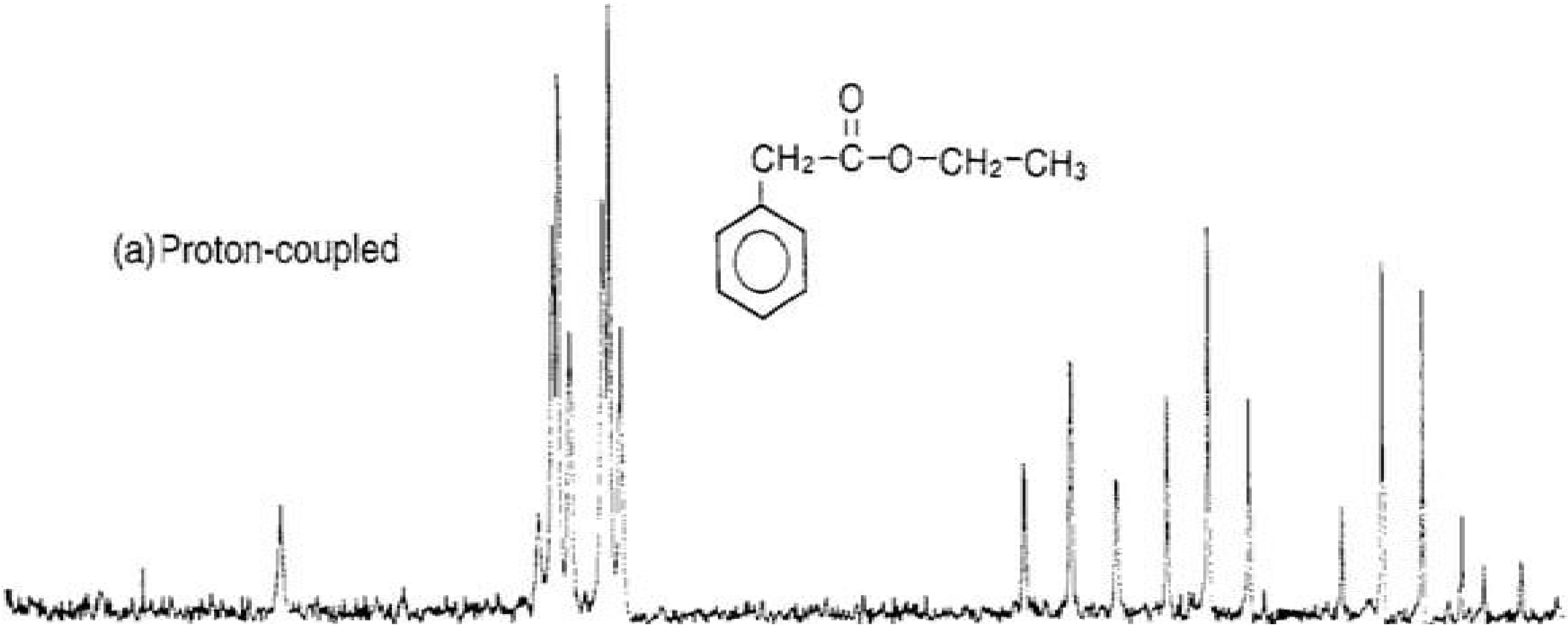
It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.

^{13}C will magnetically couple with attached protons and adjacent protons.

Coupling constant is large

These complex splitting patterns are difficult to interpret.

Proton-coupled



Proton Spin Decoupling
(Broad band decoupling)

It avoid spin-spin splitting of 13C lines by 'H nuclei.

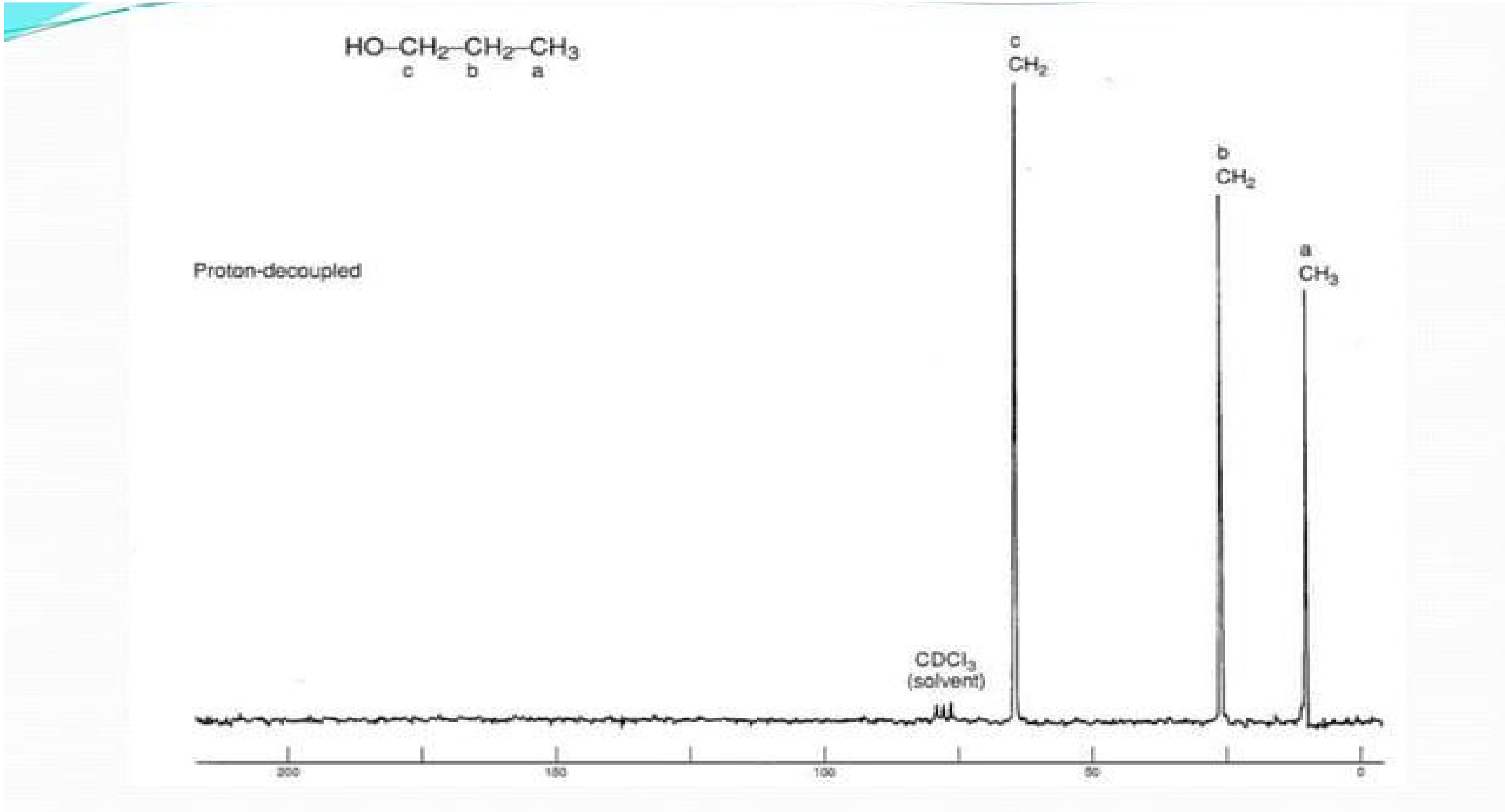
To simplify the spectrum, protons are continuously irradiated with "noise,"(broad band radiofrequency) signal **so they are rapidly flipping.**

The carbon nuclei see an average of all the possible proton spin states.

Thus, each different kind of carbon gives a single, unsplit peak

Coupling constant = 0

Proton Spin Decoupling



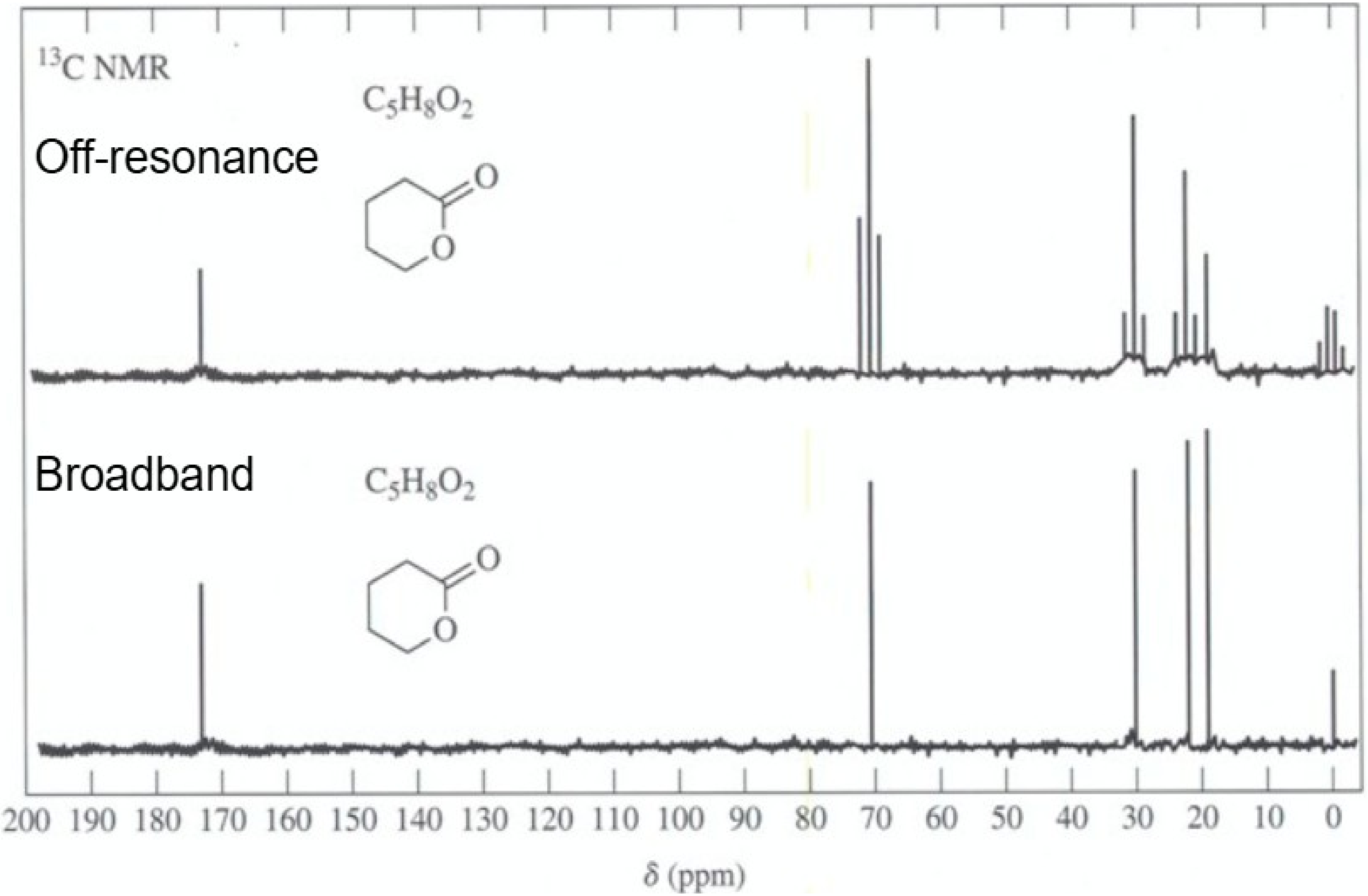
Off-Resonance Decoupling

^{13}C nuclei are split only by the protons attached directly to them.
Coupling constant is small

The *N* + 1 rule applies: a carbon with *N* number of protons gives a signal with
N + 1 peaks.

Off-resonance decoupling is rarely used because it often produces overlapping peaks that are difficult to interpret.

Off-Resonance Decoupling



DEPT 13C NMR Spectroscopy

a broadband-decoupled 13C spectrum does not provide infor mation regarding the number of protons attached to each carbon atom in a compound. This information can be obtained through a variety of recently developed techniques, one of which is called distortionless enhancement by polarization transfer (DEPT)

DEPT makes it possible to distinguish between signals due to CH3, CH2, CH, and quaternary carbons. That is, the number of hydrogens attached to each carbon in a molecule can be determined

DEPT 13C NMR Spectroscopy

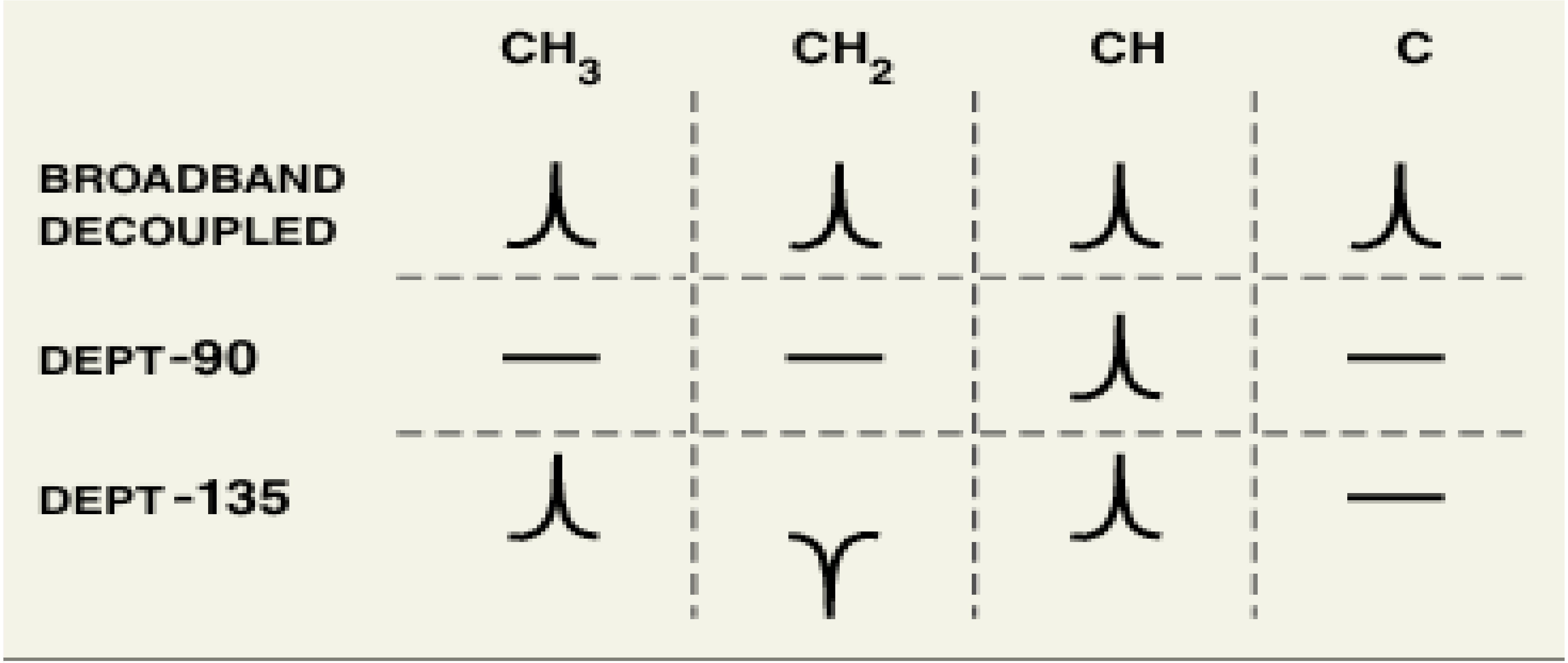
A DEPT experiment is usually done in three stages.

The first stage is to run an ordinary spectrum (called a broadband-decoupled spectrum) to locate the chemical shifts of all carbons.

Next, a second spectrum called a DEPT-90 is run, using special con ditions under which only signals due to CH carbons appear. Signals due to CH3, CH2, and quaternary carbons are absent.

Finally, a third spectrum called a DEPT-135 is run, using conditions under which CH3 and CH resonances appear as positive signals, CH2 resonances appear as negative signals—tha is, as peaks below the baseline—and quaternary carbons are

DEPT 13C-NMR



DEPT 13C-NMR

6-methyl-5-hepten-2-ol :

Part (a) is an ordinary broadband-decoupled spectrum, which shows signals for all eight carbons.
Part (b) is a DEPT-90 spectrum, which shows only signals for the two CH carbons.
Part (c) is a DEPT-135 spectrum, which shows positive signals for the two CH and three CH3 carbons and negative signals for the two CH2 carbons